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Industrial Waste Treatment and Disposal . . . AT THE GOVERNMENT SYNTHETIC RUBBER PLANTS, LOS ANGELES COUNTY, CALIF.

The government synthetic rubber plants in the Los Angeles area were faced with many difficult waste-disposal problems because of high population density and consequent low tolerance for disposal of liquid, gaseous, and solid wastes. Disposal methods currently in use were evolved during the 10-year period the plants have been in existence. All major waste-disposal problems have been solved through close cooperation between the managements of the four synthetic rubber plants and the regulatory agencies in planning and operating treatment and disposal facilities. Unusual problems involving waste tar, copper solutions, the smokeless incineration of rubber, and subsonic vibrations have also been dealt with successfully.

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INDUSTRIAL waste disposal in Los Angeles County is complicated by a high population density, a shortage of underground water supplies, and frequent temperature inversions in the atmosphere. Because of these conditions, the tolerance for disposal of liquid, gaseous, and solid wastes is low. Disposal of liquid wastes in Los Angeles County is related closely to the disposal of solid and gaseous wastes. Numerous restrictions, based on the principle that the disposal method shall not create a hazard or nuisance or cause damage, limit the possibilities for disposal.

During the years of operation of the synthetic rubber plants, process modifications have been made, and, there have been changes in the public pollution-control programs at the local, state, and federal levels. In so far as possible, the problems arising from these changes have been solved by process adjustments or by the installation of additional equipment to serve the unit producing the waste. Otherwise, modifications have been made in industrial waste treatment and disposal to meet the changing conditions. The purpose has been to provide reasonable and practical safeguards against pollution of Dominguez Channel, Los Angeles Harbor, and coastal waters of the Pacific Ocean by liquid wastes originating in the synthetic rubber plants.

The fundamental treatment facilities for industrial wastes of the government synthetic rubber plants (*2, 3*) have remained essentially unchanged. Separable oil and suspended solids are removed by settling basins. Neutralization is accomplished by mixing the various liquid wastes together or adding caustic or acid. A further reduction in oil and suspended solids is gained by filtration of the wastes through hay. Wastes which cannot be rendered nonobjectionable by settling, neutralizing, or filtration through hay can usually be treated more effectively and economically at the source, where the volume is at a minimum and the concentration at a maximum.

The original synthetic rubber plants in Los Angeles County—three butadiene plants, one styrene plant, and two GR-S plants—were placed in operation in June and July 1943. From 1947 to 1949 all except the styrene plant were shut down, but late in 1950 three plants were returned to operation. Table I lists the four plants by types, capacity, and watersheds involved in their operations.

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DISCHARGE OF TREATED WASTES

The managements of the group of plants (hereafter called the Los Angeles plants) on Vermont Avenue and Figueroa Street at Knox Street cooperated with authorities in planning and operating their waste-disposal facilities. The waste from the operations was first treated in waste-treatment units at each plant and discharged into a common drain (the Knox Street drain) and hence into the Dominguez Channel at Knox and Main Streets. In 1944 it was decided to install a spills skimming unit and a long concrete outfall pipe to Dominguez Channel (Figure 1). The work was completed in 1945 at a cost of approximately $85,000. The purpose of the skimming unit was an insurance against accidental release of oil and floating material which escapes the primary and secondary treatment units of the plants. The long concrete pipe extending beyond Main Street was installed solely for the purpose of diverting the waste water below an area originally designated as a park, and refuge and lagoon for the protection of wild life. The skimming unit still serves its original purpose. By 1948 the area protected by the pipeline had become a trash and refuse dump as a part of the smog elimination program.

Dominguez Channel is primarily a flood-control channel. In normal times it serves as an industrial waste drain for the area. The course of the channel is generally southeast, flowing from Lagunas de los Dominguez near the Los Angeles rubber plants to Sepulveda Boulevard and Alameda Streets and then in a southerly direction to the East Basin of the Los Angeles Harbor. The course is approximately 6.5 miles. The channel has been used as an industrial waste drain for a number of years.

On November 29, 1945, the County granted a permit to the Los Angeles plants to discharge treated liquid waste into Dominguez Channel. It was stipulated in the permit that the effluent shall not create any of the following conditions:

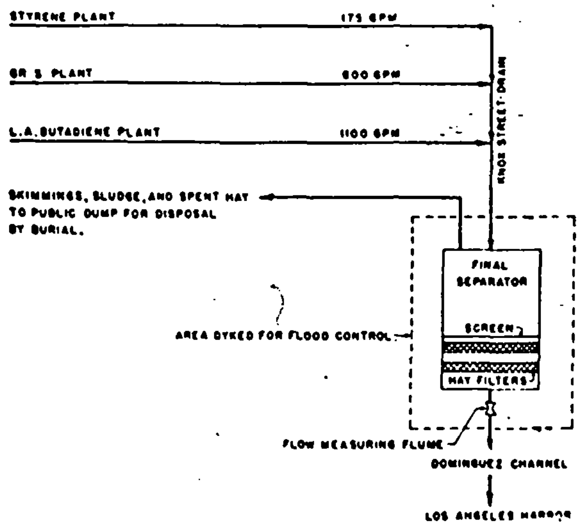


Figure 1. Knox Street Drain and Skimming Unit at Dominguez Channel

Objectionable deposits of sludge or other materials in Dominguez Channel.

Concentration of toxic wastes in sufficient quantity to endanger public health, or to affect the use of lands in the vicinity for cattle raising or other agricultural purposes.

Creation of odors to the extent that they are a public nuisance.

Discharge of oil, grease, waxes, and fats in such quantity as to create a nuisance or menace to the public safety.

Pollution of ground water to the extent that its usefulness is affected.

Damage to public or private structures or property.

Decided coloration.

The following standards were established, with the understanding that they are subject to change in the light of experience.

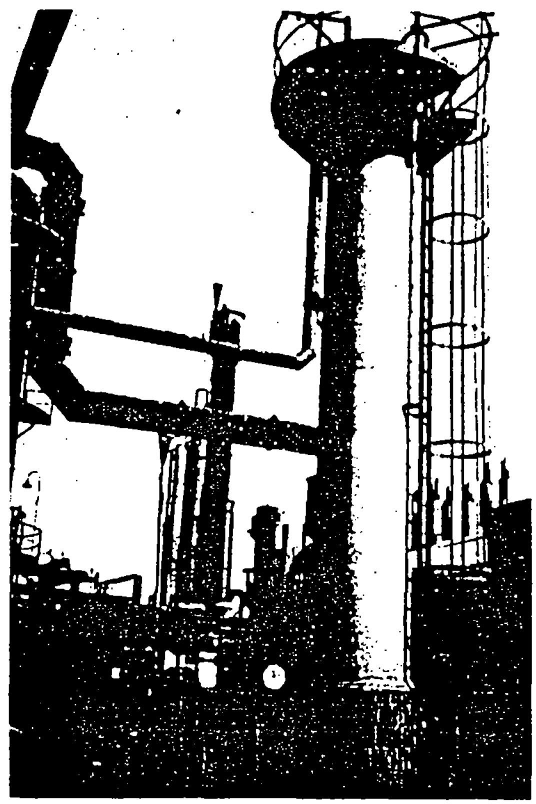
1. Settleable solids, in general, not to exceed 1.0 ml. per liter.
2. Oil, grease, fats, and waxes, not to exceed 25 mg. per liter.
3. Garbage or domestic sewage, none.
4. Acidity and alkalinity, pH 6.5 to 10.0.
5. Toxic ingredients (cyanides, phenols, metallic salts, etc.), in less than toxic concentration.
6. Temperature, not to exceed 140° F.

A standard applied subsequently stipulated that the sulfide content should not exceed 1.0 p.p.m.

Difficulty with suspended solids was experienced up to the plant shutdowns of 1947. The pH of the combined streams from the Los Angeles plants differed sufficiently from the tributary streams to cause aluminum hydroxide and iron hydroxide to flocculate in the Knox Street drain. Consequently, effluent discharged to Dominguez Channel frequently exceeded the specified maximum of 1.0 ml. per liter. Some of the floc precipitated in zones of slow flow in the upper end of the channel, but remained sufficiently fluid to be carried away whenever the flow was increased by higher drainage rates or storm water. At the time the plants were reactivated in 1950, no visible floc deposits remained. Following reactivation, iron salts were eliminated from the effluent as described below. Improved pH control at the plants contributing aluminum salts decreased the quantity of aluminum hydroxide floc formed in the combined stream in the Knox Street drain to the extent that the specified maximum of 1.0 ml. per liter of settleable solids is met at nearly all times.

The oil specification of 25 mg. per liter maximum has been exceeded at times, chiefly because of the characteristics of one waste stream. This stream is produced continuously at a rate of 400 gallons per minute, or approximately 20% of the total flow entering the Knox Street drain. The entire stream enters the treatment unit as a water-oil emulsion, and is passed upward through a sand bed 4 feet thick to coalesce the oil, and thence to a standard API gravity separator. Because of unknown factors, oil removal is not equally effective at all times. Although the search continues, a reasonably economical and effective method for oil removal has not yet been found.

The requirement of no garbage or domestic sewage has been met at all times by the plants, through use of separate sanitary sewer systems as indicated on the flow diagrams. During one brief period in 1946, however, garbage coming from a goose ranch situated on the north side of the open section of the Knox Street drain was found in the Knox Street basin. When it was explained to the rancher that county regulations did not permit

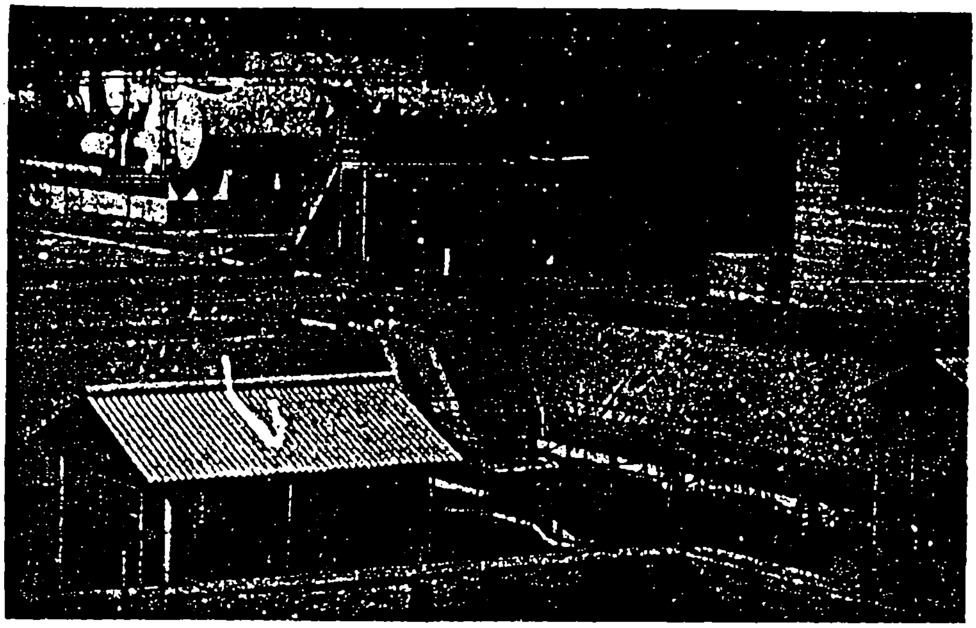


Steam Stripper for Removing Odor from Liquid Waste at El Segundo

TABLE I. PLANTS OF GOVERNMENT RUBBER PROGRAM IN LOS ANGELES COUNTY

Location of Plant	Plant Operator	Type of Plant	Approx. Prod. Capacity, Short Tons/Year	Water Course at Site	Final Receiving Body of Water
Los Angeles, Calif.	Midland Rubber Corp.	GR-S	81,000 long tons	Dominguez Channel	Los Angeles Harbor (Pacific Ocean)
	Shell Chemical Corp.	Butadiene	56,000[a]	Dominguez Channel	Los Angeles Harbor (Pacific Ocean)
	Dow Chemical Co.	Styrene	57,000	Dominguez Channel	Los Angeles Harbor (Pacific Ocean)
El Segundo	Standard Oil Co. of California	Butadiene	[a]	Pacific Ocean	Pacific Ocean

[a] Combined capacity of Shell Chemical Corp. and Standard Oil Co. of Calif. plants.



Secondary Basins for Additional Separation within GR-S Plant

garbage, no further unwelcome contributions of household garbage, deceased geese, or goose cleanings were received.

Control of pH of liquid wastes within the specified range is essential to good practice in waste disposal. In general, most of the pH difficulties involve disposal of acidic wastes. Alkaline wastes which do not contain other objectionable components are useful for neutralizing acidity. Excess spent caustic is held in storage for adjusting the effluent pH whenever the need arises in the Los Angeles plants.

In the copolymer plant the hydrogen cycle zeolite softener was changed over to sodium cycle softening and thus eliminated the drainage of acidic regeneration wastes into the sewer. The styrene plant installed a hot-process lime-soda softening to obtain boiler feedwater with a low silica content. This process change resulted in the shutdown of a hydrogen cycle zeolite softener and eliminated the drainage of acidic regeneration wastes into the sewer.

An important part of the pH problem is the treatment and disposal of alkaline copper wastes from the product purification unit of the Los Angeles butadiene plant. The copper was removed originally by acidifying the waste and agitating with air in the presence of scrap iron. While this treatment reduced the copper content to an acceptably low level, the treated wastes were acidic and contained iron salts. On adjusting the pH of the effluent to the desired range of 6.5 to 10.0, iron hydroxide was formed. This contributed to suspended solids content of the effluent, which was considered objectionable. Through the assistance and cooperation of Los Angeles County authorities, an alternative disposal method was developed, which consists of draining untreated alkaline copper-bearing wastes into the sanitary sewer. The quantity of liquid, pH, and copper content are subject to appropriate limitations to prevent any adverse effects in the sewage treatment plant or in the sewers. The tolerance for copper in any sewage treatment plant is low, but the flow of sanitary sewage through this particular treatment plant is so great that a rather large quantity of copper can be accepted without affecting operation of the digesters. Shortly after the alternative disposal method was placed in operation, a definite improvement was noted in the characteristics of remaining wastes, which are drained into Dominguez Channel. The pH fell within the desired range most of the time. Copper was eliminated from the channel and the deposition of insoluble material in the bed of the channel was decreased.

Two toxic ingredients in the Knox Street effluent are chromates and *tert*-butyl catechol. Copper, which was formerly present in concentrations of 1 to 2 p.p.m., was eliminated from the effluent drained to Dominguez Channel in 1951. Chromates are used in treating circulating cooling water, and enter the sewer system as cooling tower blowdown. The concentration is too low (15 to 50 p.p.m. as sodium dichromate) to prevent the growth of algae or bacteria in the circulating cooling water without the addition of

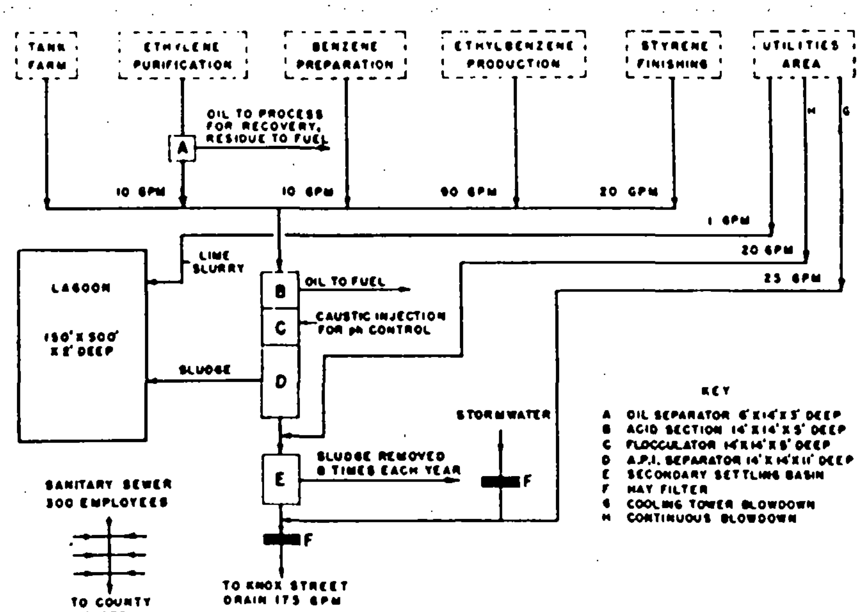


Figure 2. Facilities for Treatment of Liquid Waste at Los Angeles Styrene Plant

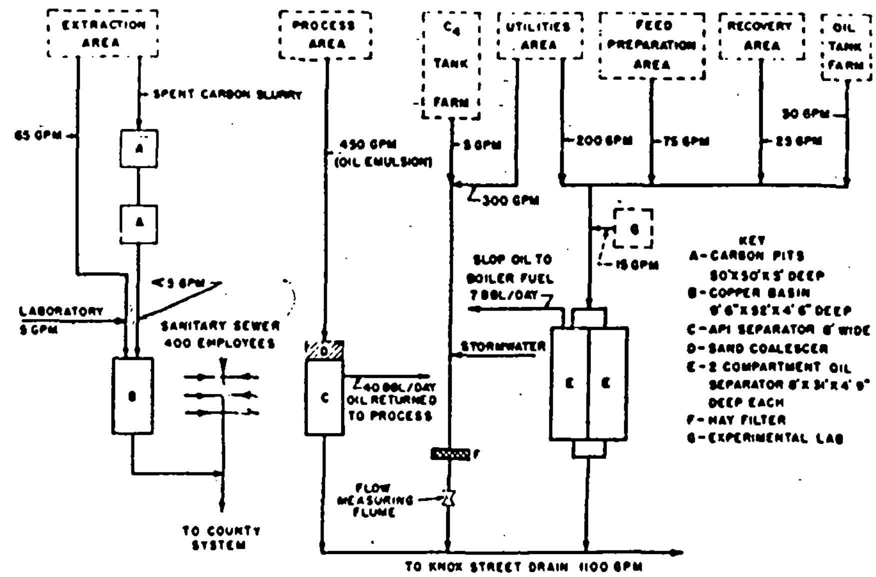


Figure 3. Facilities for Treatment of Liquid Waste at Los Angeles Butadiene Plant

discharged into sewers of the County Sanitation Districts of Los Angeles County (Figure 2).

Waste waters from ethylene and benzene purification, ethylbenzene production, ethylbenzene cracking, and styrene finishing are discharged into the process sewer terminating at the final separators. These wastes and tar recovered from the styrene *finishing* and benzene purification have caused complex waste-treatment and disposal problems. The solutions of the two problems are included in this report.

One of the manufacturing operations at the styrene plant resulted in the production of an oily sludge containing salts. The sludge could not be burned because that would have created a serious air-pollution problem. It could not be drained into the sewer system because the oil could not be separated in the settling basin. There were no dumps in Los Angeles County which could take this sludge. It would have been possible to barge the material to sea, but because of multiple handling and distances involved, this method would have been costly. As a temporary measure, the sludge was held in storage pending development of a suitable disposal method. A method was eventually developed that involved separating the sludge into two fractions: an oil that could be used for boiler fuel without creating any new problems, and another fraction, an approximately 30% aqueous solution of aluminum chloride, which was oil-free, relatively odorless, and very effective as a weed killer. A sufficiently large unit was installed to process all sludge held in storage within a reasonable time in addition to processing current production. The excess capacity was useful at a later date when the plant production was increased, and the sludge output became correspondingly

chlorine. According to Ellis (*1*), goldfish tolerated 100 p.p.m. of potassium dichromate for 108 hours, but 500 p.p.m. was fatal in 72 hours. As the cooling tower blowdown amounts to only 15% of the total effluent, it has been assumed that the hazard of draining an effluent containing less than 10 p.p.m. of chromate (as sodium dichromate) is slight. A small amount of *tert*-butyl catechol is used as an oxidation inhibitor in an intermediate material, but is removed and discarded prior to subsequent processing. The concentration in the total effluent is estimated to be not more than 0.013 p.p.m. No data are available regarding the toxicity of *tert*-butyl catechol, but a potency at least 100 times that possessed by chlorine or phenol would be required to produce any deleterious effects. It is not probable that *tert*-butyl catechol possesses such a high potency. Other toxic materials which may be present in the effluent, such as chlorine, bromine, ammonia, hydrocarbons, and metallic salts, are never present in toxic concentrations.

The temperature standard of 140° F. maximum is met at all times. The actual temperature is normally not more than 10° above atmospheric.

The sulfide content of all materials processed is so low that this ion has never been detected in the effluent.

Typical data for effluent entering Dominguez Channel are:

Suspended solids, ml. per liter	0.9
Oil, p.p.m	23
pH	8.1
Threshold odor	20

STYRENE PLANT

All liquid process wastes of the Los Angeles styrene plant after treatment and storm water collected on the plant area after passage through hay filters are discharged into the Knox Street drain. The sanitary sewage is

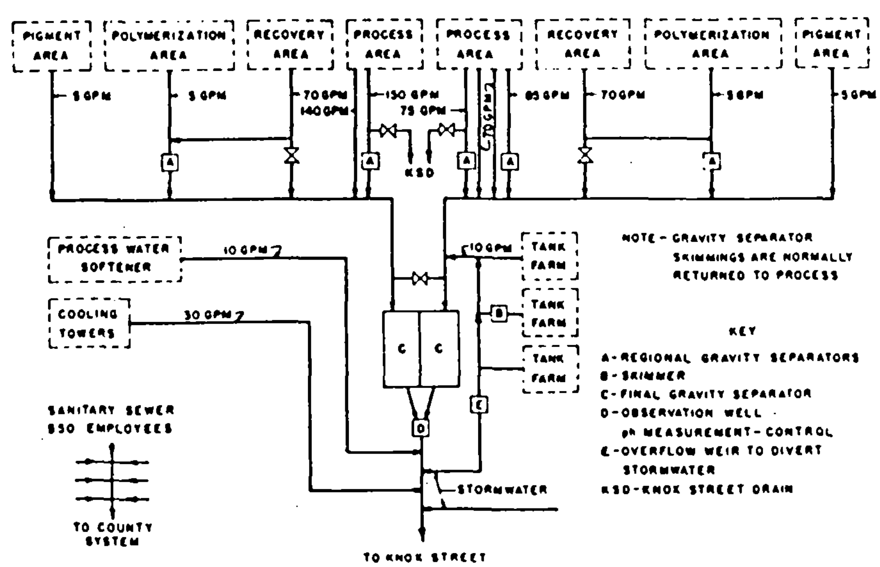


Figure 4. Facilities for Treatment of Liquid Waste at Los Angeles GR-S Plant

Knox Street Spills Skimming Unit

greater. Although the unit eliminated a difficult waste-disposal problem, it is not considered now to be a part of the waste-disposal facilities. It is deemed an extension of, and integral with, the manufacturing process.

Figure 2 indicates a multiple treatment unit which has achieved a marked reduction in the content of oil and suspended solids of the major liquid waste stream.

Originally, a single settling basin was employed to remove floating oil and aluminum hydroxide precipitate. This simultaneous separation resulted in oily floc of the same density as water in the separator effluent. Stepwise separation was accomplished by the installation of an additional basin. Acidic oily liquid waste is now settled in the first basin, where the oil is skimmed off. The effluent from this basin enters a mixing chamber, is neutralized with waste alkaline sodium aluminate solution, and flows into the second basin. Aluminum hydroxide precipitates in the second basin and is removed. The effluent from the second basin contains practically no turbidity and no visible oil. The sludge from the separators is removed and placed on sludge beds.

The waters from decanters in the ethylbenzene cracking units are subjected to distillation in order to recover volatile materials. The stripped condensate is returned to the steam plant as make-up water. Jet condenser water of the process is returned to the cooling water system.

LOS ANGELES BUTADIENE PLANT

The handling of the copper wastes of the plant is reported above. All other process wastes after treatment are discharged into the Knox Street drain. The copper wastes and sanitary sewage are discharged into the county of Los Angeles sewer system. All storm water runoff by-passes the gravity separators but passes through hay filters before entering the Knox Street drain (Figure 3).

Steam condensate from the dehydrogenation process in the production of crude butadiene is the major plant waste requiring treatment. The stream is a fairly stable emulsion. This waste is passed through a sand coalescer, where intimate contact with particles of sand frees the emulsified oil and enables the separation to be made in the gravity separator which follows the sand coalescer. About 40 barrels of oil per day are separated from this waste and returned to the process. The separator effluent is discharged to the Knox Street drain.

Wastes from the utilities area, together with wastes from the feed purification and gas recovery areas, are discharged into a sewer line that leads to two primary basins in parallel. Sludge accumulating in these basins is trucked away at yearly intervals. About 7 barrels per day of slop oil is skimmed off these basins and sent to the boiler house for use as fuel.

GR-S PLANT

Originally the present (copolymer) plant operated as two plants. These units were shut down in July 1947 and September 1949 and reopened as one plant in December 1950. The plant is designed along typical copolymer lines and is divided into the following principal production areas: pigment, polymerization, recovery, and process. The plant has been modernized to produce cold rubber, oil GR-S masterbatches, and carbon black-GR-S masterbatches in addition to the regular types and limited quantities of regular and cold latex.

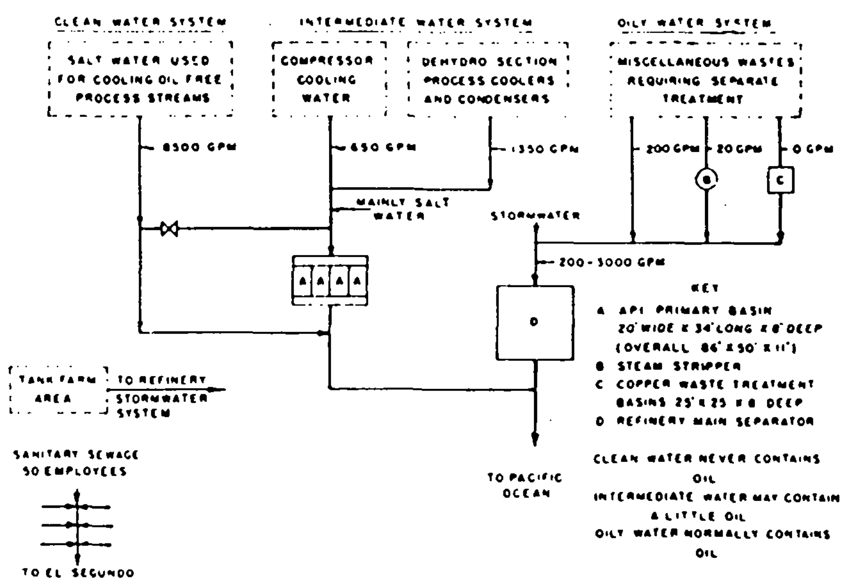
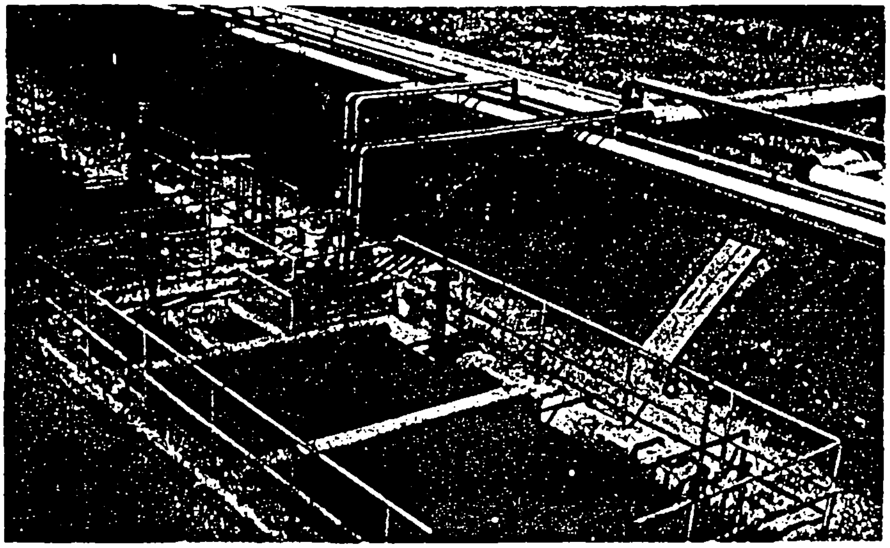


Figure 5. Facilities for Treatment of Liquid Waste at El Segundo Butadiene Plant

In 1946 new regional sumps and final separators were provided and some of the original facilities were modified. Upon reactivation in 1950 all the industrial waste facilities were placed in operation (Figure 4).

All process wastes, after regional and final treatment in gravity separators, are discharged into the Knox Street drain. Sanitary wastes are discharged into the sewer system of the county of Los Angeles. Most of the storm water is discharged into the Knox Street drain, and only a part of it passes through the final separators serving the plant.

Potential wastes from the pigment area include soaps, antioxidants, modifiers, and auxiliary chemicals. Wastes from this area are discharged directly to the final separator.



Settling Basin

Oil removal in the basin is followed by neutralization and flocculation to produce a sparkling clear effluent at the styrene plant

Regional separators are provided for treating the combined wastes from the polymerization and recovery areas. Waste waters from these areas may contain latex, polymer, and styrene. Any latex reaching these separators is coagulated and removed. Floating materials are removed from the surface of the impounding liquid during normal operations. The effluent is discharged into drains leading to the final separator.

Drains from the process areas discharge into area separators. Rubber crumbs and latex received by the separators are removed by skimming. These units also receive the waste coagulants of acidulated brine. Wash water from the Oliver filters used in processing rubber crumb in production is discharged to the final separators.

There are two final separators, each serving a part of the plant, and interconnected so one may be used when the other is being cleaned. Floating materials are removed daily and sludge from the bottom is removed twice a year.

Drains from the tank farm of the plant receive regional separation and then are discharged into the final separator. Clarified wastes from this unit are discharged into the Knox Street drain.

In 1952 an additional process separator was installed for clarification of liquid waste from carbon black masterbatch coagulation. The effluent from this separator is discharged to the final separator.

In 1952 an incinerator was installed to burn precoagulum from strainers and piping without the emission of smoke. Personnel of the Air Pollution Control District gave assistance and cooperation throughout every phase of the project.

EL SEGUNDO BUTADIENE PLANT

In 1947 the liquid waste system for the El Segundo butadiene plant was revised. The present system provides for the separation of wastes into clean water, intermediate water, oily water, copper solutions waste, foul water or quench water, and sanitary sewage (Figure 5).

Salt water used for cooling water in clean systems is discharged directly to the main drain to the ocean. The estimated flow is 8500 gallons per minute. The main drain also receives the storm water directly. The intermediate water, which is mainly salt water and may be contaminated with oil, amounting to approximately 2000 gallons per minute, passes through an API separator. The effluent is discharged to the main drain to the ocean. Oily water (including storm water), varying from 200 to 3000 gallons per minute depending on rainfall, is discharged into the main refinery separator adjacent to the butadiene plant.

Under present operations the El Segundo plant sends its crude butadiene to the Los Angeles plant; hence, the copper ammonium acetate process of butadiene purification is not used. The plant has facilities for the collection and purification of copper solution drips and spills. The copper can be removed by steaming. The clear liquid can be discharged to the oily waste sewer. The sludge from the decomposition can be disposed of by burial in locations where the quality of underground waters will not be jeopardized.

Odors emanating from aqueous waste may give rise to various difficulties. In one instance a foul water of about 20 gallons per minute from quench water drains produced a characteristic aroma that was detectable some distance from the point of discharge of the main waste water drain of the plant. This problem was solved by steam stripping the waste and returning the stripper tops to process. The stripper bottoms, which are substantially odor-free, are drained to the main sewer discharging into the ocean. The odor is no longer detectable, even at the point of discharge.

The sanitary sewage is discharged into the municipal system of the city of El Segundo.

This plant also had another problem. It is generally recognized that disturbingly loud noises of a continuous or repetitious nature will in time lead to demands by the public for abatement. Less generally recognized is the fact that subsonic vibrations

TABLE II. INSTALLED VALUE OF SANITARY AND INDUSTRIAL WASTE FACILITIES

Waste Facilities	Value
Liquid	
Sanitary sewerage	$134,000
Pipelines, drains, and ditches	
For industrial wastes	474,000
For surface and storm water	421,000
Waste treatment and disposal facilities	751,000
Solid	62,000
Gas	310,000
Total	$2,152,000

transmitted through the atmosphere may create a nuisance as great as though they were audible.

In one particular instance, three large cycloidal-type positive rotary blowers were used to supply low pressure air for process use. An electrostatic precipitator was used to remove dust and debris from the intake air. The purified air then entered an intake tunnel which served as a suction header for the three blowers, which were driven at a fixed rate by electric motors. Consequently, pulsations in the intake air occurred at a constant frequency. The air column in the intake tunnel was in resonance. The subsonic vibrations thus generated rattled the walls and windows of homes adjacent to the plant. Plate glass windows in stores vibrated audibly within a radius of one mile.

The problem was eliminated by installing a reinforced concrete block building around the air intake, in order to draw the air through a series of baffles. The dimensions and placement of the baffles were designed to damp out pulsations of the same frequency generated by the blowers. Subsonic vibrations in the atmosphere may not be an air pollutant, but public reaction was the same as if they were.

In November 1952 the sanitary and industrial waste facilities installed and in use at the plants were valued at $2,152,000, an increase of $787,000 since March 1946. Table II summarizes data as to liquid, solid, and gaseous facilities.

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Disposal of California Winery Wastes

The major problems concerned with the disposal of California winery wastes result, in large measure, from the tremendous volume of brandy stillage produced in an intermittent, seasonal operation. The stillage, estimated to average about 200 gallons per ton of grapes crushed, is extremely variable in potential putrescibility. Therefore, land disposal by intermittent irrigation is the best method of disposal at present although complete treatment of the stillage can be effected by a combination of neutralization, anaerobic digestion, and biological oxidation.

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ADEQUATE disposal of liquid winery wastes has been a continuously perplexing problem since the revival of the industry in California in 1933. In the years immediately following resumption of large scale production, the pollution of streams with concentrated winery wastes was acute (*4, 9*). When the further discharge of concentrated liquid winery wastes to the rivers was prohibited by the Division of Fish and Game, state of California, use of deep ponds or lagoons became standard practice, even though this gave rise to widespread odor nuisances resulting from anaerobic fermentation of the wastes. Abatement of these odors has become of immediate concern to many California vintners. It is anticipated that odor control and other requirements for sanitary disposal of liquid winery wastes will be magnified with time because of the continual increases in the population of the state.

NATURE OF THE WASTES

Winery wastes may, for convenience, be defined as liquid, semiliquid, and solid residues which are removed from the wine by natural or artificial means during the process of vinification. These residues, for the most part, are natural to the grape. A few arise from other sources. The following kinds are encountered:

Liquid	Semiliquid	Solid
Waste wash water Brandy distillery wastes Condenser water Stillage (still-slop)	Lees Dessert wine Table wine Refrigeration Clarification and filtration sediments (bentonite, Filter-Cel, etc.)	Pomace Cream of tartar deposits (argols or wine stone)

It has always been customary to utilize certain of these wastes in making by-products. The argols are collected and used for manufacture of tartrate or tartaric acid. (During World War II tartrates were recovered from other sources, such as pomace, refrigeration lees, and stillage. This recovery is not economical at present.) The pomace may be used as a soil mulch or dried and used for prepared stock feed. Lees from table or dessert wines generally are used for the recovery of brandy, but their distillation adds to the over-all waste-disposal problem created by the enormous volumes of brandy distillery wastes, together with the other liquid wastes of the wine industry in California.

VOLUME OF BRANDY DISTILLERY WASTES

It is difficult to estimate the total volume of brandy distillery wastes, either for an individual winery or for the whole California industry. The volume of these wastes depends upon a great many variables: the seasonal character of the industry, the tonnage of grapes crushed, the ratio of wine to brandy made from the grapes that are crushed, and variations in winery and distillery operation and practice, particularly those used to produce the wine "distilling material" from which neutral brandy for fortification is derived.

Every effort is made to obtain fortifying spirit from the materials at hand. Brandy distillery wastes, therefore, may originate from distillation of distilling materials produced from pomace and lees, as well as wines. The volume, as well as the chemical composition of the stillage, will vary significantly from time to time, although the majority of the spirit used is derived from distilling material produced from wines rather than the grape residues.